Chemical Communications

NUMBER 11/1966 8 JUNE

Shapes of Tris(trimethylstannyl)-amine, -phosphine, -arsine, and -stibine

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RECENT interest in the structures of $(H_3Si)_3N$,[1] $(H_3Si)_3P$,[2] and $(H_3Ge)_3P$,[3] has prompted us to investigate similar tin compounds. As it has not yet been possible to synthesise the derivatives $(H_3Sn)_3X$, we have examined the corresponding trimethylstannyl compounds $(Me_3Sn)_3X$, where X = N, P, As, Sb. These derivatives have been prepared in high yield by the reaction:

$$3Me_3Sn{\cdot}NMe_2 + XH_3 \rightarrow (Me_3Sn)_3X + 3Me_2NH$$

and have been characterised by elemental analyses and proton magnetic resonance spectroscopy (confirming the equivalence of 27 protons).

The vibrational spectra of these compounds have been investigated with a view to the possible determination of the shape of the XSn_3 skeleton. For a pyramidal configuration having C_{3v} symmetry, the totally symmetric modes are active in both infrared and Raman spectra (A_1 species are polarised, all other species must be depolarised), while in C_{3h} (planar skeleton, but no C_2 axes or σ_v planes if the methyl groups are considered), the totally symmetric A' modes are active only in the Raman spectrum.

We have obtained infrared spectra (Perkin-Elmer 521, 4000—250 cm.$^{-1}$ region) and Raman spectra (Perkin-Elmer L.R-1 using 6328Å excitation with a sample of about 2 ml. in a multi-reflecting cell at 25—30°) of all the compounds in the liquid phase. Our results indicate that all the observed polarised Raman lines have equivalents in the infrared spectra. This clearly establishes that all the compounds are pyramidal, in spite of the fact that Courtauld models allow construction of the nitrogen compound only in the planar configuration. For the nonplanar model to be correct, this suggests that the Sn–N bonds are unusually long, and therefore weak; an explanation consistent with the high reactivity observed for Sn–N derivatives.[4]

Our preliminary comparative analysis of the infrared and Raman spectra has enabled us to identify frequencies characterising the symmetric stretching modes of the XSn_3 groups as highly polarised Raman lines at 514, 290, and 209 cm.$^{-1}$ for the N, P, and As compounds respectively. In each of these pyramidal molecules, the symmetric stretching mode must involve motion of the central atom, so that without a complete normal-co-ordinate analysis (for which a knowledge of the out-of-plane angles is required), it is impossible to separate the mass effect from the effect upon these frequencies of changing Sn–X bond strength. Support for our assignment is provided by the occurrence at 322 cm.$^{-1}$ of the analogous symmetric stretching mode in $(H_3Ge)_3P$,[3] but the corresponding NSi_3 and PSi_3 frequencies at 496 and 414 cm.$^{-1}$ respectively,[2] are of little value for comparison since in these planar silyl compounds no motion of the central atom is involved. However, it is worth noting that the asymmetric stretching modes for these silicon compounds which do involve motion of the central atoms, occur at 987 and 455 cm.$^{-1}$ respectively. This comparison suggests particularly weak Sn–N bonds in $(Me_3Sn)_3N$, in keeping with our earlier conclusion.

The asymmetric stretching modes of the XSn_3 skeletons are more difficult to assign with certainty, due to the depolarised and weak nature of their Raman lines, but detailed comparison of all our spectra indicates that these occur at 672,[5] 351, and 233 cm.$^{-1}$ for the N, P, and As compounds respectively. The spectra of all compounds studied were essentially identical at frequencies above the 672 cm.$^{-1}$ line, indicating that all other skeletal modes give lower frequencies. The related Sn–N derivative, $Sn(NMe_2)_4$, appears to have its SnN_4 asymmetric stretching mode at 538 cm.$^{-1}$, providing a further example of a low-frequency Sn–N stretching mode, though this evidently is at variance with a recent assignment[6] of the Sn–N stretch in *N*-trimethylstannylaniline at 843 cm.$^{-1}$

(*Received, April* 21*st*, 1966; *Com.* 258.)

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[2] G. Davidson, E. A. V. Ebsworth, G. M. Sheldrick, and L. A. Woodward, *Chem. Comm.*, 1965, 122, and *Spectrochim. Acta*, 1966, **22**, 67.

[3] S. Cradock, G. Davidson, E. A. V. Ebsworth, and L. A. Woodward, *Chem. Comm.*, 1965, 515.

[4] K. Jones and M. F. Lappert, *Organometallic Chem. Rev.*, 1966, **1**, 67, and references cited therein.

[5] K. Sisido and S. Kozima, *J. Org. Chem.*, 1964, **29**, 907, gave 728 cm.$^{-1}$ as the ν_{as}(Sn–N) from $(Me_3Sn)_3N$, but they had neither Raman spectra nor the analogous P and As compounds for comparison.

[6] E. W. Randall, J. J. Ellner, and J. J. Zuckerman, *Inorg. Nuclear Chem. Letters*, 1966, **1**, 109.